Photocycloadditions of four homologous 2-(cycloamino)-propenenitriles to 1-acetonaphthone

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Abstract
2-(Cycloamino)propenenitriles H₂C=C(CN)N(CH₂)n (n = 4, 5, 6, 7) are added to triplet π,π*-excited 1-acetonaphthone forming 8b-acetyl-2-(cycloamino)-1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-2-carbonitrides as well as 1-acetyl-9-(cycloamino)-1,4-dihydro-1,4-ethanonnaphthalene-9-carbonitrides. Regio- and stereoselectivity of the photocycloadditions and the special role of the cyclobuta[a]naphthalene adducts in the initial stage of the photoadditions are discussed.

Keywords: 1-Acynaphthalenes, α-cyanoenamines, light-sensitive photocycloadducts, π,π* triplet reactivity, selectivity phenomena

Introduction

So-called captodatively substituted¹⁻³ alkenes, especially 2-aminopropenenitriles such as 2, undergo a variety of photocycloadditions to fused arenes.⁴ 2-Morpholinopropenenitrile (2)⁵ had been used preferentially in our earlier studies for its crystallinity and easy purification by crystallization, and for its easy removal from reaction mixture residues by vacuum sublimation.

It had earlier been demonstrated that 2 may readily undergo a [4+2]-cycloaddition to phoetoexcited 1-acetonaphthone (= 1-(1-naphthyl)ethanone, 1) – a prototypical 1-acylnaphthalene – giving rise to rel-(1R,4R,9R)-1-acetyl-1,4-dihydro-9-morpholino-1,4-ethanonaphthalene-9-carbonitrile (3).⁶,⁷ This reaction was later shown to proceed via a low-lying excited triplet state of 1.⁸,⁹ There also was indication for the formation of a minor [2+2]-adduct, namely 8b-acetyl-1,2,2a,8b-tetrahydro-2-morpholinocyclobuta[a]-naphthalene-2-carbonitrile (4)⁷ (Scheme 1). The latter compound had been found sensitive to thermal and light-induced (313 nm) reversal to the starting materials.⁷ The very low yield of 4 is in contrast to various other inter- and intramolecular [2+2]-photocycloadditions to naphthalenes, especially naphthonitriles,¹⁰,¹¹ while 1,4-photocycloadditions are rare for these compounds.
Our previous finding that 1-naphthonitrile (5), when excited in the presence of 2, does not give rise to any 1,4-adduct, instead the two cyclobutanaphthalenes 6 and 7 were formed, is in analogy to related cases in the literature (Scheme 2).

Mode switching to practically exclusive 1,2-[2+2]-photocycloaddition of 2 and the analogous 2-(1-piperidinyl)propenitrile (9b, see below) is observed for 4-R-substituted (R = OCH₃, CH₃, F, CN) acetonaphthones, whereas this mode is suppressed with 2-R-substituted (R = OCH₃, CH₃) acetonaphthones.

In contrast to the rich meta-photocycloaddition chemistry of benzene, only a few examples of intermolecular and intramolecular 3+2-photocycloadditions of alkenes to the naphthalene skeleton have been reported in the literature. Any direct 3+2-photocycloadditions of 1 (or of any 1-acyl analogues to that) to α-cyanoenamines have not been observed by us. However, when the 1,4-adduct 3 was irradiated with 254 nm light, a formal 3+2-photoadduct 8 was obtained (Scheme 3) via a di-π-methane rearrangement.
Scheme 3

Close inspection of the connectivity of 8 reveals that this compound could never have been formed via a direct [3+2]-photocycloaddition of 2 to 1, but it can well be taken as the formal [3+2]-photocycloadduct of 2 to 2-acetonaphthone!

The 1,8-mode of [3+2]-photocycloaddition of alkenes to the naphthalene ring, as reported for naphthalene-1,4-dicarboxylic acid diesters,25,26 has not been observed so far for α-cyanoenamines and related captodative alkenes. From all of this, it has been demonstrated that photocycloadditions of captodative alkenes, especially α-cyanoenamines, to 1-acyl-naphthalenes (acyl = CHO, COCH₃, COPh, COOCH₃) and analogues thereof are governed by the following selectivities:

1. Site selectivity: Only the acyl bearing ring is affected. Also, the acyl carbonyl groups of the 1-acylnaphthalenes have never been involved in Paterno-Büchi reactions27 with α-cyanoenamines.
2. Mode selectivity: Only the 1,2-[2+2]- and the 1,4-[4+2]-photocycloaddition modes but no 1,3-[3+2]-photoadditions have been observed so far.
3. Addition direction selectivity (“regioselectivity”): The head (acylnaphthalene) to tail (alkene) mode has been followed in all [2+2] and [4+2] cases.
4. Stereoselectivity: The donor group (predominantly a cyclic amino group) is preferentially oriented syn to the unaffected benzenoid ring in the 1,4-photocycloadducts, while the relative orientation (donor-syn or donor-anti, respectively, to the unaffected benzenoid ring) in the 1,2-photocycloadducts is less pronounced. In either case three new stereocenters are generated, and for obvious reasons, a pair of diastereomers (the C-9-epimers in the 1,4-[4+2]-addition and the C-2-epimers in the 1,2-[2+2]-addition) are to be expected as products.
5. Diastereoselectivity: Has been demonstrated earlier for the [4+2]-photocycloaddition of 1 to two chirally labeled 2-aminopropenenitriles.4,28

It was felt that the extension of the model photocycloaddition of 2 to 1 to a series of closely related α-cyanoenamines 9a-d with similar electronic properties but gradually different steric requirements could cast some light on the mode, regio-, and stereoselectivities of these photocycloadditions. Thus, alkenes 9a-d, the cyclic amino substituent of which (1-pyrrolidinyl, 1-piperidinyl, hexahydro-1H-azepin-1-yl, and octahydro-1-azocinyl) is in the following frequently called the “donor”, were chosen for addition to photoexcited 1.
The energy of the lowest excited ($\pi,\pi^*$) triplet state of 1 has been reported to be $E_T = 236$ kJ mol$^{-1}$,$^{29}$ its lifetime at room temperature in benzene solution is reported to be $\tau = 2 \times 10^{-4}$ s.$^{30}$ Ns-laser flash photolysis experiments$^8$ had revealed that tetramethyl diazetine 1,2-dioxide (TMDD,) $E_T = 146$ kJ mol$^{-1}$ $^{31,32}$ quenches the T-T absorption (480 nm) of triplet 1 with $k_q = 52.3 \times 10^8$ M$^{-1}$ s$^{-1}$. Alkenes 2, 9$a,b,c$, do quench triplet excited 1, the rate constants being below the diffusion controlled limit, $10^{-8} x kq / M^{-1} s^{-1} = 3.5 \pm 0.2$ for 2, $28.3 \pm 0.3$ for 9$a$, $9.0 \pm 0.1$ for 9$b$, and $25.0 \pm 0.2$ for 9$c$ in methanol$^8$. Thus, in irradiated solutions containing 1, 2 (or 9$a$) and TMDD, the latter successfully competes with the alkene in quenching triplet excited 1.

**Results and Discussion**

**Preparative scale photocycloadditions**

Preparative scale photolysis ($\lambda > 280$nm), run to 42-45% conversion of 1, led to yields of 60-85% (referred to converted 1, after refining by crystallization) of 1,4-adducts 10$a$-$d$ (Scheme 4).

![Scheme 4]

**Scheme 4**
Table 1. Structurally relevant 300.1 MHz $^1$H NMR data of products 10 and 11 (δ in ppm, $J$ in Hz).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Comp.</th>
<th>10-H$_A$</th>
<th>10-H$_B$</th>
<th>$^2$$J_{AB}$</th>
<th>2-H</th>
<th>3-H</th>
<th>4-H</th>
<th>$^3$$J_{2,3}$</th>
<th>$^4$$J_{2,4}$</th>
<th>$^3$$J_{3,4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CDCl$_3$</td>
<td>10a</td>
<td>2.19</td>
<td>2.03</td>
<td>12.6</td>
<td>6.89</td>
<td>6.76</td>
<td>4.31</td>
<td>7.8</td>
<td>0.7</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>CDCl$_3$</td>
<td>10b</td>
<td>2.22</td>
<td>1.91</td>
<td>12.5</td>
<td>6.91</td>
<td>6.74</td>
<td>4.50</td>
<td>7.7</td>
<td>0.5</td>
<td>6.5</td>
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<td>3</td>
<td>CDCl$_3$</td>
<td>10c</td>
<td>2.26</td>
<td>1.92</td>
<td>12.5</td>
<td>6.89</td>
<td>6.71</td>
<td>4.47</td>
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<td>0.5</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>CDCl$_3$</td>
<td>10d</td>
<td>2.19</td>
<td>2.13</td>
<td>12.7</td>
<td>6.91</td>
<td>6.70</td>
<td>4.50</td>
<td>7.8</td>
<td>0.8</td>
<td>6.4</td>
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<td>5</td>
<td>C$_6$D$_6$</td>
<td>10a</td>
<td>2.05</td>
<td>2.01</td>
<td>12.6</td>
<td>6.46</td>
<td>6.40</td>
<td>3.85</td>
<td>7.8</td>
<td>1.1</td>
<td>6.3</td>
</tr>
<tr>
<td>6</td>
<td>C$_6$D$_6$</td>
<td>10b</td>
<td>2.10</td>
<td>1.89</td>
<td>12.5</td>
<td>6.48</td>
<td>6.39</td>
<td>4.01</td>
<td>7.7</td>
<td>0.8</td>
<td>6.5</td>
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<td>7</td>
<td>C$_6$D$_6$</td>
<td>10c</td>
<td>2.16</td>
<td>1.92</td>
<td>12.5</td>
<td>6.48</td>
<td>6.39</td>
<td>3.96</td>
<td>7.7</td>
<td>0.02</td>
<td>6.5</td>
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<tr>
<td>8</td>
<td>C$_6$D$_6$</td>
<td>10d</td>
<td>2.10</td>
<td>2.06</td>
<td>12.7</td>
<td>6.46</td>
<td>6.35</td>
<td>3.98</td>
<td>7.8</td>
<td>1.0</td>
<td>6.4</td>
</tr>
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<td>9</td>
<td>CDCl$_3$</td>
<td>11a</td>
<td>2.31</td>
<td>1.95</td>
<td>12.7</td>
<td>6.83</td>
<td>6.56</td>
<td>4.29</td>
<td>7.8</td>
<td>0.7</td>
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<tr>
<td>10</td>
<td>CDCl$_3$</td>
<td>11b</td>
<td>2.34</td>
<td>1.85</td>
<td>12.5</td>
<td>6.81</td>
<td>6.51</td>
<td>4.43</td>
<td>7.9</td>
<td>1.3</td>
<td>6.1</td>
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<td>CDCl$_3$</td>
<td>11c</td>
<td>2.36</td>
<td>1.85</td>
<td>12.5</td>
<td>6.78</td>
<td>6.50</td>
<td>4.40</td>
<td>7.9</td>
<td>0.7</td>
<td>6.0</td>
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<td>CDCl$_3$</td>
<td>11d</td>
<td>2.33</td>
<td>1.94</td>
<td>12.6</td>
<td>6.81</td>
<td>6.51</td>
<td>4.41</td>
<td>7.8</td>
<td>1.2</td>
<td>6.0</td>
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<td>13</td>
<td>C$_6$D$_6$</td>
<td>11a</td>
<td>2.29</td>
<td>1.79</td>
<td>12.5</td>
<td>6.52</td>
<td>6.11</td>
<td>3.95</td>
<td>7.8</td>
<td>0.8</td>
<td>6.0</td>
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<td>14</td>
<td>C$_6$D$_6$</td>
<td>11b</td>
<td>2.33</td>
<td>1.67</td>
<td>12.7</td>
<td>6.54</td>
<td>6.01</td>
<td>4.05</td>
<td>7.8</td>
<td>0.8</td>
<td>6.0</td>
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<td>15</td>
<td>C$_6$D$_6$</td>
<td>11c</td>
<td>1.74</td>
<td>1.27</td>
<td>6.01</td>
<td>4.01</td>
<td>7.9</td>
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<td>16</td>
<td>C$_6$D$_6$</td>
<td>11d</td>
<td>2.35</td>
<td>1.82</td>
<td>12.7</td>
<td>6.52</td>
<td>6.04</td>
<td>4.03</td>
<td>7.8</td>
<td>6.0</td>
<td></td>
</tr>
</tbody>
</table>

Entries in normal type refer to spectra of isolated samples, entries in italic type to satellite spectra in spectrograms of the mother liquors of the main products 10. Bold type: Signals selected for following the reaction by $^1$H NMR.

The donor-syn geometry of these main adducts has been unambiguously established by single-crystal X-ray structure analyses for 10a, 10b, and 10c. Since the $^1$H chemical shifts and the coupling constants for the 10-H$_2$ AB system and 2-H, 3-H, and 4-H of 10d in both CDCl$_3$ and C$_6$D$_6$ solution matched very well those of 10a-c (Table 1), a donor-syn geometry can safely be assumed as well for 10d. Also, the $^{13}$C chemical shifts of compounds 10a-d are quite close (Table 2).
Table 2. $^{13}$C($^1$H) chemical shifts (δ/ppm) of photoproducts 10a-d in CDCl$_3$

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Cycloamino methylene groups</th>
<th>Other carbon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α</td>
<td>β</td>
</tr>
<tr>
<td>10a</td>
<td>48.9</td>
<td>23.3</td>
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<tr>
<td>10b</td>
<td>49.4</td>
<td>25.7</td>
</tr>
<tr>
<td>10c</td>
<td>50.1</td>
<td>26.2</td>
</tr>
<tr>
<td>10d</td>
<td>50.0</td>
<td>27.8</td>
</tr>
</tbody>
</table>

The configuration of compounds 10 is also reflected in the 1D NOE intensity enhancements found for compound 10c as an example (see Table 3). Especially the enhancement noted for the multiplet of the aromatic protons 5, 6, and 7 upon irradiation of the multiplet ascribed to the quasi-equatorial hexahydroazepin-1-yl α-protons indicates a syn-orientation of this cycloamino group to the benzenoid ring (entry 5). This effect requires a brief comment.

Table 3. 1D NOE intensity enhancements observed for compound 10c in C$_6$D$_6$ (δ/ppm, assignments)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Signal irradiated$^a$</th>
<th>Signals enhanced$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.92 10-H$_B$</td>
<td>2.16 10-H$<em>A$; 2.40-2.50 N(CH$</em>{qax}$)$_2$</td>
</tr>
<tr>
<td>2</td>
<td>1.96 COCH$_3$</td>
<td>6.48 2-H; 6.77 8-H</td>
</tr>
<tr>
<td>3</td>
<td>2.18 10-H$_A$</td>
<td>1.92 10-H$_B$</td>
</tr>
<tr>
<td>4</td>
<td>2.41-2.50 N(CH$_{qax}$)$_2$</td>
<td>0.94-1.36 (CH$_2$)$_4$; 1.92 10-H$<em>B$; 2.50-2.60 N(CH$</em>{qeq}$)$_2$; 3.96 4-H</td>
</tr>
<tr>
<td>5</td>
<td>2.50-2.60 N(CH$_{qeq}$)$_2$</td>
<td>0.96-1.34 (CH$_2$)$<em>4$; 2.41-2.50 N(CH$</em>{qax}$)$_2$; 3.96 4-H, 6.82-6.93 5-, 6-, 7-H</td>
</tr>
<tr>
<td>6</td>
<td>3.96 4-H</td>
<td>2.50-2.60 N(CH$_{qeq}$)$_2$; 6.39 3-H</td>
</tr>
<tr>
<td>7</td>
<td>6.39 3-H</td>
<td>3.96 4-H</td>
</tr>
</tbody>
</table>

$^a$ qax = quasi-axial, qeq = quasi-equatorial

While the 1-piperidinyl α-protons in 10b give rise to two distinct multiplets (in C$_6$D$_6$ at δ 2.20-2.30 and 2.42-2.55 ppm), the one at lower field was assigned to the equatorial, the one at higher field to the axial α-H-atoms.$^{36}$ Compounds 10a,c in the same solvent show almost baseline separated N(CH$_2$)$_2$ multiplets, the branch of which at higher field being assignable to the
quasi-axial (qax), the branch at lower field to the quasi-equatorial (qeQ) α-H-atoms. For 10d, this near-splitting is observed only in CDCl₃ but not in C₆D₆. For 10e, separate irradiation of the qax and qeQ α-proton signals gives different patterns of NOE enhancements (see Table 3, entries 4 and 5).

**Identification of the byproducts**

The mother liquor residues, when subjected to ¹H NMR investigation in freshly prepared CDCl₃ solution, did show, besides residual starting materials 1 and 9a-d, additional (albeit partly resolved) signal sets for minor byproducts to which structures 11-13, all being isomers of 10, were assigned primarily on the basis of their ¹H NMR data as follows:

a) For better resolution it had turned out to be advantageous to inspect also the ¹H NMR spectra of the mother liquor residues of 10a-d in C₆D₆ as solvent.

b) Two related signal sets were assigned to two 2-epimeric 1,2-[2+2]-adducts 12a-d and 13a-d each showing an AX system for the geminal protons at C-1, and two styrene-like olefinic protons coupled to a third one assigned to the bridgehead 2a-H (Table 4);

c) A third signal set very similar to those of 10a-d, except that the AB system of the latter (Δν/J = 1-8) had been replaced with a borderline AX pattern (Δν/J = 8-12 in CDCl₃ and 12-15 in C₆D₆), and two olefinic protons (2-H, 3-H), not conjugated to the benzenoid ring and both coupled to the bridgehead H-4 (Table 1, entries 9-12 and 13-16).

d) Additionally, in separate experiments starting materials 1 and 9a,c were irradiated deliberately to low conversion to obtain the well crystallizing byproducts 13a,c preferentially, so their complete ¹H and ¹³C{¹H} NMR spectra could be obtained separately without overlap with signals from other products present.

The configuration assignments of byproducts 12 and 13 were made as follows: from Table 4 the relevant chemical shifts in CDCl₃ {C₆D₆} for 1-Hₐ, 1-Hₓ and 2a-H can be taken as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>1-Hₐ</th>
<th>1-Hₓ</th>
<th>2a-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>12c</td>
<td>3.42</td>
<td>2.41</td>
<td>3.64</td>
</tr>
<tr>
<td>13c</td>
<td>3.25</td>
<td>2.69</td>
<td>3.21</td>
</tr>
</tbody>
</table>

The cis-vicinal CN group deshields 37,38 1-Hₐ in 12c (compared to that in 13c) but 1-Hₓ in 13c (compared to that in 12c). In both compounds 1-Hₓ experiences a high field shift through the anisotropy of the benzenoid ring, this effect is, however, partially compensated by the influence of the cis-vicinal CN group in 13c but not in 12c. The latter group somewhat deshields 2a-H in 12c but not in 13c. These findings allow to discriminate between structures 12c and 13c.

For 13c, also NOE’s (Table 5) are in accord with the donor-anti geometry. Irradiation into the α-methylene multiplet (2.40-2.56 ppm) enhances not only the (CH₂)₄ multiplet but also the signals at 3.21 2a-H, 3.25 1-Hₐ, and 5.81 ppm 3-H. Further relevant effects (signal irradiated / signal enhanced): 2.69 1-Hₓ / 6.93 8-H; 3.21 2a-H / 5.81 3-H. In view of the very similar ¹H NMR data (see Table 4), compounds 13a,b,d and 12a,b,d may be assigned the donor-anti and donor-syn geometries, respectively.
Table 4. Structurally relevant 300.1 MHz $^1$H NMR data of byproducts 12 and 13 (δ in ppm, J in Hz) as far as they could be extracted from the spectrograms.

![Diagram of molecules 12a-d and 13a-d](image)

| Entry | Solvent | Comp. | 1-H_A | 1-H_X | $|J_{AX}|$ | 2a-H | 4-H | 3-H | $J_{3,4}$ | $J_{2a,4}$ | $J_{2a,3}$ |
|-------|---------|------|-------|-------|-------|------|-----|-----|--------|--------|--------|
| 1     | CDCl$_3$ | 12a  | 3.42  | 12.8  |        | 6.56 | 5.76| 9.8 | 1.4    | 4.8    |
| 2     |         | 12b  |       |       |        | 6.58 | 5.74| 10.0| 1.9    | 4.3    |
| 3     |         | 12c  | 3.42  | 2.41  | 12.1  | 3.64 | 6.58| 5.73| 9.8    | 4.9    |
| 4     |         | 12d  |       |       |        | 6.58 | 5.78| 10.3| 1.1    | 4.9    |
| 5     | C$_6$D$_6$ | 12a  | 3.57  | 12.3  | 2.0   | 6.16 | 5.30| 9.9 | 1.6    | 4.9    |
| 6     |         | 12b  |       |       |        | 6.20 | 5.35| 9.5 | 0.8    |        |
| 7     |         | 12c  | 3.41  | 2.14  | 12.2  | 3.25 | 2.5 | 6.17 | 5.27   | 10.0   | 0.6    | 4.8    |
| 8     |         | 12d  | 3.46  | 2.11  | 12.3  | 2.3  | 6.15 | 5.28 | 9.7    | 1.1    | 5.1    |
| 9     | CDCl$_3$ | 13a  | 3.35  | 2.70  | 14.5  | 3.32 | 0.8 | 6.71 | 5.82   | 9.8    | 5.7    |
| 10    |         | 13b  | 3.26  | 2.67  | 12.1  | 3.22 |     | 6.70 | 5.78   | 9.7    | 5.6    |
| 11    |         | 13c$_a$ | 3.25 | 2.69  | 12.0  | 3.21 | 0.7 | 6.69 | 5.81   | 9.8    | 5.7    |
| 12    |         | 13d  |       |       |        | 6.69 | 5.81| 9.8 | 5.7    |        |
| 13    | C$_6$D$_6$ | 13a  | 3.36  | 2.50  | 12.1  | 2.98 | 1.0 | 6.39 | 5.47   | 9.8    | 2.4    | 5.6    |
| 14    |         | 13b  | 3.28  | 2.47  | 12.0  | 2.86 | 0.6 | 6.38 | 5.36   | 9.7    | 5.6    |
| 15    |         | 13c  | 3.26  | 2.48  | 12.0  | 2.92 | 0.8 | 6.38 | 5.43   | 9.7    | 5.6    |
| 16    |         | 13d  | 3.33  | 2.46  | 12.2  | 2.98 | 0.8 | 6.38 | 5.47   | 9.8    | 2.1    | 5.5    |

Entries in normal type refer to spectra of isolated samples, entries in italic type to satellite spectra in spectrograms of the mother liquors of the main products 10. Bold type: Signals selected for following the reactions by $^1$H NMR.

$^a$ An additional coupling of $^4J_{1-H_X,2a} = 0.8$ Hz is observed.
Table 5. 1D NOE intensity enhancements observed for compound 13c in CDCl₃ (δ/ppm, assignments)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Signal irradiated</th>
<th>Signals enhanced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.52-1.73 (CH₂)₄</td>
<td>2.40-2.59 N(CH₂)₂; 3.21 2a-H</td>
</tr>
<tr>
<td>2</td>
<td>2.40-2.56 N(CH₂)₂</td>
<td>1.50-1.75 (CH₂)₄; 3.21 2a-H, 3.25 1-H_A; 5.81 3-H</td>
</tr>
<tr>
<td>3</td>
<td>2.69 1-H_B</td>
<td>3.25 1-H_A, 6.93 8-H</td>
</tr>
<tr>
<td>4</td>
<td>3.21 2a-H</td>
<td>2.40-2.59 N(CH₂)₂; 2.69 1-H_B; 5.81 3-H</td>
</tr>
<tr>
<td>5</td>
<td>3.26 1-H_A</td>
<td>2.69 1-H_B</td>
</tr>
</tbody>
</table>

The close similarity of the third low intensity ¹H NMR signal set, especially the resonances for 10-H_AH_B and 2-H, 3-H, 4-H with those of the main products 10a-d, suggested the third byproduct to be the 9-epimer 11a-d of the latter. Compared with the situation in 10a-d, the upfield shift exerted by the benzenoid ring on H_A is in part counterbalanced by the influence of the vicinal nitrile group, while the downfield shift of that group on 10-H_B in 10a-d is no longer present in 11a-d, thus 10-H_A resonates at lower and 10-H_B at slightly higher field than in the ¹H NMR of 10a-d.

The following observation is noteworthy in this context: When CDCl₃ solutions of pure isolated 10a,c,d (but not of 10b!) were kept standing for periods between several days and a week, additional signal sets identical to those assigned to 11a,c,d built up. This suggested that compounds 10a,c,d underwent C9-epimerisation forming 11a,c,d by opening and re-closure of either the C4-C9 bond or (probably catalyzed by traces of acid) the C9-CN bond generating the close ion pair 14 which, when at least partially separated, may return to either 10 or 11 (Scheme 5).

![Scheme 5](image-url)

a: n = 4; c: n = 6; d: n = 7
**Time dependent product distribution**

Mode selectivity (i.e., 1,2- vs. 1,4-cycloaddition) had earlier been surmised to be time dependent for the photocycloadditions of several captodative alkenes to 1.\(^4\) Since a related mode selectivity has been experimentally demonstrated for the photocycloaddition of 5-fluoro-1,3-dimethyluracil to naphthalene\(^39\), and time dependent product ratios in intramolecular [2+2]-photocycloadditions of 2-alkenylsubstituted 1-naphthonitriles have been reported,\(^40\) such time dependence studies were found desirable also for the photocycloadditions of 9a-d to 1. Thus, 5 mm (o.d.) NMR tubes were charged with 0.6 mL samples of C\(_6\)D\(_6\) solutions 0.1 M in both 1 and 9a-d and exposed to the same broad-band UV irradiation as used for the preparative scale runs. 300 MHz \(^1\)H NMR spectra were scanned at appropriate regular time intervals and the concentrations of residual starting material 1 and the four cycloadducts 10, 11, 12, and 13 were determined by signal intensity integration at selected chemical shifts (9.15 ppm for 1, for products 10, 11, 12, and 13 see Tables 1 and 4). Integrals were taken as measures of percentages and have not been calibrated. As in other studies applying the same NMR methodology, the experimental error is to be assumed as ± 1\(^%\) \(^41\) or ± 1-2\(^\%\).\(^42\) This error may significantly increase since the NMR integration method tends to overestimate the major diastereomer in a mixture when the \(dr\) is 100:1 or even larger.\(^42\) In spite of any experimental errors or methodological shortcomings, our experimental results suffice to show a clear trend. Since no further products were observed during the total time span of the experiments, the proportions of residual starting material 1 and products 10, 11, 12, and 13 were expressed in % with the sum of all percentages of said components at any time regarded as 100\(^\%\). Time-resolved concentration changes are shown in Figure 1 for the photocycloadditions of 9a-d to 1. For 9b a separate determination for both 1,2- and both 1,4-adducts was impossible, thus only the sum of the percentages of the epimeric mixtures of the 1,4-adducts 10b,11b and 1,2-adducts 12b,13b, respectively, could be determined.
Figure 1. Small-scale irradiations of 1-acetonaphthone (1) in the presence of alkenes 9a (a), 9b (b), 9c (c), and 9d (d). The percentages of starting material 1 and products 10, 11, 12, and 13 versus time were followed by $^1$H NMR in C$_6$D$_6$. 
From Figure 1 it can be taken that the curves for both the epimeric 1,4-adducts 10a,c,d (donor-syn) and 11a,c,d (donor-anti) gradually climb although with clearly different slopes, whereas the plots for the 1,2-donor-anti products 13a,c,d initially climb faster than those for the main products 10a,c,d but go through a maximum after 50, 60, and 40 min, respectively, and have dropped to a few percent or close to zero at the end of the experiment. This clearly demonstrates the donor-anti 1,2-photocycloaddition forming 13a,c,d to be faster by a factor of approximately 1.9, 2.4, and 2.7, respectively, at low conversion and that the 1,4-photocycloadducts 10, 11 are formed independently of the 1,2-photoadducts 12, 13 and not consecutively from these.

The reason for this is to be sought in the enhanced light sensitivity of the 1,2-cycloadducts 12, 13 with their styrene-like chromophore which causes their photo-retro-cleavage to the starting materials, while the 1,4-photocycloadducts 10 and 11 remain stable towards the incident light and accumulate. Reversibility of intramolecular [2+2]-photocycloadditions of double bonds to the 1-cyanonaphthalene system, preceding the [3+2]-photocycloaddition, have also been observed by Mizuno et al.22,23

The course of the observed photocycloadditions
Monochromatic (313 nm) excitation of a common equimolar solution of 1 and model compound 2 in acetonitrile had shown a marked decrease of the absorbance between 250 and 290 nm and no isosbestic points over the wavelength range 240-380 nm in the reaction spectrum, demonstrating that only products of lower absorbance than that of either starting material are produced. The graphical evaluation of the reaction spectrum gave linear absorbancy-time and absorbancy diagrams43. These findings point to a simple reaction of the type A + B —> C (or several parallel reactions of that type).
Aspects of regio- and stereoselection (facial selectivity) have been discussed before\textsuperscript{4,7,14} and will be addressed here only briefly (Scheme 6). In both of the parallel reaction modes ([2+2]- and [4+2]-photocycloadditions) two relative orientations (donor-\textit{syn} and donor-\textit{anti}) of the reactants determine the stereochemical outcome and are apparently maintained all the way to the final products 10-13. Whether or not triplet excitation of is is followed by formation of a (even very short lived) exciplex, in turn followed by formation of a biradical, cannot be answered yet. The only transient observed in a ns-laser flash photolysis experiment (308 nm excimer laser of 7 ns pulse width and 10 mJ energy) with 1 in the presence of model compound 2 in acetonitrile and with 9a-c in methanol is the first excited (\(\pi,\pi^*\)) triplet state of 1 which is quenched by 2, 9a-c,
TMDD and also by methyl viologen (MV\textsuperscript{2+})\textsuperscript{8}. The latter reagent allows to detect biradicals indirectly\textsuperscript{44} but no such biradical could be detected either spectroscopically or by quenching.

Indeed biradicals like 15/15' with one captodatively\textsuperscript{1-3} substituted and one benzylic/allylic terminus are attractive intermediates at least in the [4+2]-photocycloaddition but still have to be regarded as speculative. Because of their likely fleeting existence it is doubtful that they interconvert by rotation around the C9-C10 bond, since products 10 and 11 cannot be interconverted thermally and there are no direct interconversions of [2+2]- and [4+2]-photoadducts either. All photoproducts decay to starting materials upon thermal activation.

A direct photointerconversion of products 12/13 to 10/11 may be ruled out by analogy to the photochemical behavior of the model compound 4\textsuperscript{7} (see Scheme 1). When irradiated (313 nm) in acetonitrile solution, 4 is completely decomposed into 1 and 2 as demonstrated by the rapid increase of absorbance of the solution prior to a slow but marked decrease when the [4+2] photocycloadduct is formed. If 4 had been transformed directly into 3, the absorbance of the solution had to decrease from the beginning of the experiment. The finding that acidic impurities in CDCl\textsubscript{3} may catalyze the conversion of 10a,c,d into 11a,c,d at ambient temperature (Scheme 5) does not require biradical intermediates. This transformation, however, indicates that compounds 11 are thermodynamically more stabler than their 9-epimers 10.

Conclusions

Photoexcited 1-acetonaphthone (1) adds a series of a-cyanoenamines 9a-d in two parallel reaction modes, namely, the 1,4-[4+2]- and the 1,2-[2+2]-addition. Since in either case a mixture of two epimers is formed, a total of four independent cycloadditions is taking place. As can be seen at low conversion, the order of rate of these is: 1,2 donor-\textit{anti} (leading to 13) > 1,4 donor-\textit{syn} (leading to 10) > 1,2 donor-\textit{syn} (leading to 12) > 1,4 donor-\textit{anti} (leading to 11). While the main products isolated in 60-85% yield from preparative scale irradiations reaching 42-45% conversion of starting material 1 are the donor-\textit{syn} 1,4-[4+2]-cycloadducts 10a-d, their 9-epimeric donor-\textit{anti} 1,4-[4+2]-cycloadducts have been identified by \textsuperscript{1}H NMR spectroscopy only to be present in 3% (11a), 6% (11c), and 4% (11d) in the crude photolysates. The donor-\textit{anti} 1,2-[2+2]-photocycloadducts 13a,c,d are noteworthy since they are at low conversion present in the reaction mixtures in significantly higher concentrations than those of the main photoadducts 10a,c,d, but later, as the screening effect of the starting material 1 decreases, undergo light induced cleavage back to the starting materials, while the concentrations of both 1,4-photocycloadducts 10 and 11 increase. While only two (13a,c) of the donor-\textit{anti} [2+2]-cycloadducts 13 could be isolated and their structures unambiguously be determined, byproducts 12a-d and 13b,d could be identified from their individual \textsuperscript{1}H NMR signal sets only. Any distinct differences in mode or stereoselectivity in the photocycloadditions of 9a-d to 1, dependent on the
ring size of the donor group of 9, have not been observed, however. Just gradual differences could be detected by 1H NMR-following of the photocycloadditions.

Experimental Section

General. Mps have been determined on a Kofler hot stage microscope. – IR spectra have been recorded from liquid films or KBr disks on a Perkin-Elmer 983 spectrophotometer. – Mass spectrometry: An AMD 604 instrument (EI mode) using 70 eV ionization energy and a direct inlet system, adjusted to the temperatures given, was used. – NMR spectra were recorded on a Bruker WM 300 instrument operating at 300.1 MHz for 1H and 75.5 MHz for 13C, with TMS as internal standard. Abbreviations: s singlet, d doublet, m multiplet. – UV spectra were taken on a Perkin Elmer Lambda 40 instrument. – Elemental analyses for C, H, and N were obtained on a Carlo Erba Elemental Analyzer model 1106.

1-Acetonaphthone (1) was purchased from Aldrich and distilled, bp 75-80 °C /0.15 Torr. 1H NMR (300.1 MHz, CDCl3): δH 2.70 (3H, s, COCH3), 7.30-8.90 (7H arom, several m, 7CH): (300.1 MHz, CDCl3): δH 2.23 (3H, s, COCH3), 7.01-7.61 (6H arom, m, 2-H to 7-H), 9.16-9.19 (1H arom, m, 8-H). UV [cyclohexane; λmax nm, (log ε)]: 211 (4.59), 2.16 (4.56), 235 (4.23), 245 (4.21), 302 (3.81), 322 (3.60). – 2-(Cycloamino)propenenitriles 9a-d were prepared as described earlier by adaption of the procedure for preparation of 2 published by Temin to prepare 9a, and the procedure for preparation of 9b by Balsubramanian et al. was used to prepare 9b-d. All samples were refined by bulb-to-bulb distillation in vacuo. IR (liquid film), 300.1 MHz 1H NMR (CDCl3) and 75.5 MHz 13C{1H} NMR (CDCl3) data have already been given in ref., and only additional physical, spectral, and analytical data are given below.

2-(1-Pyrrolidinyl)propenenitrile (9a). Bp 31 °C/0.4 Torr, lit. 58-59 °C/1.5 Torr, nD 1.4995. UV [cyclohexane; λmax nm (log ε)]: 264 (3.94). 1H NMR (300.1 MHz, CDCl3): δH 1.14-1.21 [4H, m, (CH2)2], 2.59-2.65 [4H, m, N(CH2)2], 3.77 and 4.32 (1H each, no coupling observed, 3-H2). MS (22 °C) m/z (%) = 122 (M, 96), 121(91), 94 (100), 93 (38). Anal. Calcd for C7H10N2 (122.17): C, 68.82; H, 8.25; N, 22.93%. Found: C, 69.06; H, 8.32; N, 22.82%.

2-(1-Piperidinyl)propenenitrile (9b). Bp 42 °C/0.026 Torr, lit. 100 °C/2 Torr, lit. 77 °C/1.5 Torr, nD 1.4038. UV [cyclohexane; λmax nm (log ε)]: 259 (3.79). 1H NMR (300.1 MHz, CDCl3): δH 0.95-1.22 [6H, m, (CH2)3], 2.48-2.57 [4H, m, N(CH2)2], 3.77 (1H, d, JHH 1.63 Hz, 3-HB), 4.19 (1H, d, JHH 1.63 Hz, 3-HA). MS (124 °C), m/z (%) = 136 (M, 100), 121 (29), 108 (29), 95 (33). Anal. Calcd for C8H12N2 (136.20): C, 70.55; H, 8.88; N, 20.57%. Found: C, 70.51; H, 8.93; N, 20.64%.

2-(Hexahydro-1H-azepin-1-yl)propenenitrile (9c). Bp 70 °C/0.038 Torr. UV [cyclohexane; λmax nm (log ε)]: 270 (3.78). 1H NMR (300.1 MHz, CDCl3): δH 108-1.16 [4H, m, (CH2)2], 1.20-1.30 [4H, m, (CH2)2], 2.75-2.83 [4H, m, N(CH2)2], 3.86 (1H, d, JHH 1.62 Hz, 3-HB), 4.29 (1H, d, JHH 1.62 Hz, 3-HA). MS (137 °C), m/z (%) = 150 (M, 100), 135 (56), 121 (30), 110 (24), 107
(54), 95 (47). Anal. Calcd for C₉H₁₄N₂ (150.23): C, 71.96; H, 9.39; N, 18.65%. Found: C, 72.04; H, 9.38; N, 18.79%.

2-(Octahydroazocin-1-yl)propenenitrile (9d). Bp 53 °C/0.032 Torr. UV [cyclohexane; λₘₐₓ, nm (log ε)]: 273 (3.95).

1H NMR (300.1 MHz, C₆D₆): δH 1.10-1.35 [10H, m, (CH₂)₅], 2.55-2.62 [4H, m, N(CH₂)₂], 3.86 (1H, d, |JHH| 1.59 Hz, 3-HB), 4.31 (1H, d, |JHH| 1.59 Hz, 3-HA). MS, m/z = 164 (M, 100), 149 (48), 135 (20), 121 (18), 107 (37, 96 (72), 95 (62). Anal. Calcd for C₁₀H₁₆N₂ (164.25): C, 73.13; H, 9.82; N, 17.06%. Found: C, 72.90; H, 9.96; N, 16.94%.

Preparative scale irradiations

A Philips HPK 125 W high pressure mercury lamp was used in connection with a water-cooled Duran™ immersion well (λ > 280 nm) and a cylindrical vessel with a gas in- and outlet and a magnetic stirrer. Cyclohexane solutions (170 mL) of 1-acetonaphthone (1) and alkene 9a-d (0.1 M each) were purged with Ar (99.996%) for 30 min and then irradiated for the periods given with stirring and under continuous Ar purging (for details see Table 6) whereby the mixture assumed a yellow or orange-brown color. The photolyzates were concentrated to oily residues which were diluted with hexane and stirred vigorously under ice cooling. The crude precipitates were filtered off, washed with hexane and dried. Crystallization from ethyl acetate/hexane (1:1) under ice/salt cooling gave the refined products 10a-d (see Table 6 for yields). Structurally relevant ¹H NMR data have been given in Tables 1 and 4, ¹³C{¹H} NMR data in Table 2.

Table 6. Preparative photocycloadditions of alkenes 9a-d (1.7 mmol each) to 1-acetonaphthone (1, 2.89 g, 1.7 mmol) in 170 ml of cyclohexane. Conditions and yields

<table>
<thead>
<tr>
<th>Alkene used (g)</th>
<th>Irradiation time / h</th>
<th>Conversion of 1 / %</th>
<th>Product</th>
<th>Crude yield* (g (%)</th>
<th>Refined yield* (g (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a (2.07)</td>
<td>9</td>
<td>44</td>
<td>10a</td>
<td>1.87 (85)</td>
<td>1.30 (60)</td>
</tr>
<tr>
<td>9b (2.31)</td>
<td>8</td>
<td>42</td>
<td>10b</td>
<td>1.74 (80)</td>
<td>1.33 (61)</td>
</tr>
<tr>
<td>9c (2.55)</td>
<td>20</td>
<td>45</td>
<td>10c</td>
<td>2.29 (93)</td>
<td>1.65 (67)</td>
</tr>
<tr>
<td>9d (2.79)</td>
<td>18</td>
<td>45</td>
<td>10d</td>
<td>2.49 (96)</td>
<td>2.16 (85)</td>
</tr>
</tbody>
</table>

*Yields refer to converted starting material 1.

Filtrates and washings were concentrated to dryness and subjected to ¹H NMR analysis (in CDCl₃ solution) which revealed the presence of a 1:1 mixture of both starting materials, the concentrations of which were determined by signal integration and allowed the determination of conversion of 1, on which the yields given in Table 6 are based. In addition to the signals of the main products 10, three minor signal sets were detected and assigned to the minor byproducts 11a-d (see Table 1, entries 9-16), 12a-d (Table 4, entries 1-8) and 13a-d (Table 4, entries 9-16). rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(1-pyrrolidinyl)-1,4-ethanonaphthalene-9-carbonitrile (10a). Mp 108 °C (decomp.). IR (ṽ/cm⁻¹): 2212 (CN), 1712 (C=O). UV [acetonitrile, λₘₐₓ, nm (log ε)]: 256 (2.34), 262 (2.39), 270 (2.26). ¹H NMR (300.1 MHz, CDCl₃
rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(1-piperidinyl)-1,4-ethanonaphthalene-9-carbonitrile (10b). Mp 143-144 °C (decomp.). IR (v/cm⁻¹): 2216 (CN), 1700 (C=O). UV [acetonitrile, λmax, nm (log ε)]: 256 (2.30), 262 (2.36), 270 (2.20). ¹H NMR (300.1 MHz, CDCl₃, C₆D₆): See Table 1, entries 2 and 6, and δH 1.30-1.51 {1.01-1.19} (6H, m, piperidinyl β- and γ-H), 2.52 {1.94} (3H, s, COCH₃), 2.40-2.50 {2.20-2.30} [2H, m, N(CH₃)₂], 2.62-2.75 {2.42-2.55} [2H, m, N(CH₃)₂], 6.94-6.97 {6.71-6.77} (1H arom, m, 8-H), 7.15-7.26 {6.77-6.94} (3H arom, m, 5-H, 6-H, 7-H). MS (125 °C), m/z (%) = 279 (M-HCN, 8), 2.63 (M-CH₃CO, 4), 236 (M-HCN and COCH₃, 4), 170 (C₁₂H₁₀O 1, 40), 155 (C₁₁H₇O, 43), 136 (9b, 100). Anal. Calcd for C₂₀H₂₂N₂O (306.41): C, 78.40; H, 7.24; N, 9.14%. Found: C, 78.44; H, 7.21; N, 9.06%.

rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(1-hexahydro-1H-azepin-1-yl)-1,4-ethanonaphthalene-9-carbonitrile (10c). Mp 91-92 °C (decomp.). IR (v/cm⁻¹): 2212 (CN), 1712 (C=O). UV [acetonitrile, λmax, nm (log ε)]: 255 (2.46), 262 (2.48), 270 (2.36). ¹H NMR (300.1 MHz, CDCl₃, C₆D₆): See Table 1, entries 3 and 7, and δH 1.12-1.73 {0.94-1.36} (8H, m, hexahydro-1H-azepin-1-yl β- and γ-H), 2.51 {1.96} (3H, s, COCH₃), 2.55-2.70 {2.41-2.50} [2H, m, n(CH₃)₂], 2.70-2.92 {250-2.60} [2H, m, N(CH₃)₂], 6.93-6.99 {6.75-6.78} (1H arom, m, 8-H), 7.14-7.30 {6.83-6.94} (3H arom, m, 5-H, 6-H, 7-H). MS (92 °C), m/z (%) = 293 (M-HCN, 2), 2.63 (M-CH₃CO, 0.4), 250 (M-HCN and COCH₃, 1), 170 (C₁₂H₁₀O 1, 62), 155 (C₁₁H₇O, 99), 100 (9c, 47), 127 (C₁₀H₇, 100). Anal. Calcd for C₂₁H₂₄N₂O (320.44): C, 78.71; H, 7.55; N, 8.74%. Found: C, 78.51; H, 7.56; N, 8.62%.

rel-(1R,4R,9R)-1-Acetyl-1,4-dihydro-9-(octahydroazocin-1-yl)-1,4-ethanonaphthalene-9-carbonitrile (10d). Mp 103 °C (decomp.). IR (v/cm⁻¹): 2213 (CN), 1710 (C=O). UV [acetonitrile, λmax, nm (log ε)]: 255 (2.40), 262 (2.40), 270 (2.25). ¹H NMR (300.1 MHz, CDCl₃, C₆D₆): See Table 1, entries 4 and 8, and δH 0.86-0.96, 1.08-1.32, 1.32-1.56 [2H, 4H, 4H 3m, (CH₃)₂ but 0.84-1.25] [10H, m, (CH₂)₅ -1.23], 2.51 {1.94} (3H, s, COCH₃), 2.55-2.65 [2H, m, N(CH₃)₂] and 2.65-2.80 [2H, m, N(CH₃)₂ but {2.36-2.51} [4H, m, N(CH₃)₂], 6.93-7.00 {6.72-6.78} (1H arom, m, 8-H), 7.14-7.34 {6.82-6.95} (3H arom, m, 5-H, 6-H, 7-H). MS (95 °C), m/z (%) = 307 (M-HCN, 0.2), 2.64 (M-HCN and COCH₃, 0.2), 170 (C₁₂H₁₀O 1, 95), 164 (9d, 31), 155 (C₁₁H₇O, 100), 127 (C₁₀H₇, 100). Anal. Calcd for C₂₂H₂₆N₂O (334.46): C, 79.00; H, 7.84; N, 8.38%. Found: C, 78.92; H, 7.88; N, 8.32%.

rel-(2R,2aR,8bS)-8b-Acetyl-2-(1-pyrrolidinyl)-1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-2-carbonitrile (13a). A solution of 2.55 g (15 mmol) of 1 and 1.87 g (15 mmol) of 9a in 125 mL of cyclohexane was purged with Ar and irradiated as described above for 6.5 h to 23% conversion. A crop of 640 mg (23%, based on consumed starting material as are the following yields) of 10a was directly filtered off and crystallized from ethyl acetate/hexane to give 490 mg.
(48%), mp 108 °C (with decomp.). The original filtrate, combined with the mother liquor, gave 3.50 g of a residue which was subjected to preparative layer chromatography using hexane. Besides unreacted starting materials, from a zone at Rf 0.43, 90 mg of crystals were obtained and crystallized from ethyl acetate/hexane, yielding 74 mg (7%), mp 138-140 °C. IR (v/cm⁻¹): 2200 (CN), 1705 (C=O). UV [cyclohexane, λmax, nm (log ε)]: 265 (3.77), 274 (3.77), 292 (3.37), 302 (3.29). ¹H NMR (300.1 MHz, CDCl₃): See Table 3, entry 9, and δH 1.76-1.87 [4H, m, (CH₂)₂], 201 (3H, s, COCH₃), 2.50-2.62 [4H, m, N(CH₃)], 6.91-6.96 (1H₁, m 8-H), 7.11-7.28 (3H₂, m, 5-H, 6-H, 7-H). MS (81 °C), m/z (%) = 265 (M-HCN, 1), 249 (M-COCH₃, 3), 247 (5), 170 (C₁₂H₁₀O, 1, 6), 155 (C₁₁H₂O, 17), 141 (5), 127 (17), 122 (9a, 100), 121 (10). Anal. Calcld for C₁₉H₂₀N₂O (292.38): C, 78.05; H, 6.90; N, 9.58%. Found: C, 77.99; H, 6.71; N, 9.58%.

rel-(2R,2aR,8bS)-8b-Acetyl-2-(hexahydro-1H-azepin-1-yl)-1,2,2a,8b-tetrahydrocyclobuta[a]-naphthalene-2-carbonitrile (13c). A solution of 1.70 g (10 mmol) of 1 and 1.50 g (10 mmol) of 9c in 100 mL of dry cyclohexane was purged with and irradiated under argon as described above for 4.5 h. After concentration, the residue was taken up in 50 mL of hexane and left standing at -70°C for seven days. The crystalline precipitate was washed with cold isopropanol, dried and then taken up in 1 mL of ethyl acetate to which 20 mL of hexane were added. The mixture was left at -70°C over night to give 90 mg of colorless crystals, mp 132 °C. IR (v/cm⁻¹): 2208 (CN), 1706 (C=O). UV [acetonitrile; λmax/nm (log ε)]: 224 (4.50), 267 (3.96), 308 (plateau, 3.39). ¹H NMR (300.1 MHz, CDCl₃): See Table 3, entry 11, and δH 1.50-1.75 (8H, m, hexahydro-1H-azepin-1-yl β- and γ-H), 2.01 (s, 3H, COCH₃), 2.40-2.59 [m, 4H, N(CH₂)₂], 6.91-694 (1H, m, 8-H), 7.05-7.25 (3H₂, m, 5-H, 6-H, 7-H). – ¹³C NMR (75.5 MHz, CDCl₃): δC: 24.9 (CH₃), 26.4 (2 CH₂), 28.7 (2 CH₂), 43.8 (C-1), 47.3 (C-8b), 47.5 (C-2a), 50.0 [N(CH₂)₂], 64.0 (C-2), 118.0 (CN); aryl and alkenyl CH at 121.2, 126.8, 128.6, 128.7, 129.3, 1131.1; quaternary aryl C at 131.5, 133.1; 205.4 (C=O). Anal. Calcld for C₂₁H₁₅N₂O (320.4): C, 78.71; H, 7.55; N, 8.74 %. Found: C, 78.71; H, 7.52; N, 8.70%. A crop of 1.14 g of 1 was recovered chromatographically, thus a maximum of 0.56g (33%) of 1 had reacted.

**Time dependent product distribution**

In four separate experiments, solutions (6 mL each) 0.1 M in both 1-acetonaphthone (1) and either 9a, 9b, 9c or 9d in C₆D₆, were purged for 30 min with Ar and equally distributed under Ar on ten NMR tubes (0.5 cm o. d.). The tubes were tightly stoppered, one was set aside as a blank, the other nine were affixed to the outer wall of a water-cooled immersion well and irradiated (λ >280 nm), while being externally cooled with water, with a Philips 125 W high pressure mercury lamp. At regular time intervals a sample was scanned at 300.1 MHz. The integrals at δ 9.15 ppm (for 1) and at selected δ values for the four products (see bold face entries in Tables 1 and 3) were added and the sum was taken as 100%, and the percentages of 1, 10, 11, 12, and 13 were calculated from the integrals and plotted (see Figure 1).
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